

LIQUEFACTION OF MICRO ALGAE WITH IRON CATALYST

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INTRODUCTION

Recently, carbon dioxide fixation by cultivating micro algae is being investigated. Since cultivated micro algae would be degraded into carbon dioxide, methane, and water by micro biological process, effective utilization of micro algae produced are highly required.

Production of liquid fuels from biomass have been extensively studied. Effects of hydrogen donor solvents¹ or alkali metal carbonate catalysts² on biomass conversion were reported under a hydrogen or a carbon monoxide atmosphere. Yokoyama *et al.* summarized techniques concerning the liquefaction of wood, and reported that sodium carbonate is effective catalyst for increasing the oil yield in water in the absence of reducing gas.³ More lighter oil was obtained in a high yield by the addition of organic solvents such as propanol, butanol and ethyl acetate.⁴ Dote *et al.* reported that sodium carbonate was effective catalyst for the liquefaction of *Botryococcus braunii* in water under nitrogen.⁵

In this work, we have investigated liquefaction of *Spirulina* in various organic solvents or water under a hydrogen, a nitrogen or a carbon monoxide atmosphere in the temperature range of 300-425 °C using Fe(CO)₅-S catalyst developed for the liquefaction of coal⁶ and discussed the effects of reaction conditions and catalysts on the product distribution and properties of oil.

EXPERIMENTAL SECTION

Spirulina (C 46.1; H 7.4; N 4.8; S 0.4; O 41.4 %, protein 57.5; fat 12.0; fatty acid 1.0; carbohydrate <0.5 %) was used as a micro alga. A 2.0 g of dried *Spirulina*, 8.0 g of tetralin, 1-methylnaphthalene, toluene or water and the prescribed amount of catalyst were put into a 50 mL magnetically stirred autoclave. The autoclave was pressurized to 5 MPa with hydrogen, nitrogen or carbon monoxide, and then the autoclave was heated up to a certain reaction temperature. After the reaction, products were separated by extraction with THF. THF soluble fraction was further separated into hexane-insoluble and hexane soluble (oil fraction). Gaseous products were analyzed by gas chromatography. As a catalyst, Fe(CO)₅-S (Fe 1.0 mmol, S/Fe=2) was used. Oil fractions obtained in toluene and water were analyzed by FT-IR and gel permeation chromatography. C, H, and N elemental analyses were carried out at Osaka university.

Heating values of oil fractions were estimated by equation (1). Where C, H, N, S and O are normalized to weight fractions of respective elements in oil.⁷

$$H_g = 8400C + 27765H + 1500N + 2500S - 2650O \quad [\text{cal/g}] \quad (1)$$

RESULTS AND DISCUSSION

Effect of reaction conditions in the liquefaction of *Spirulina*. Table 1 shows results of liquefaction of *Spirulina* at 350 °C for 60 min in tetralin or 1-methylnaphthalene under a hydrogen or a nitrogen atmosphere with or without a catalyst. More than 90 % of conversions and 50 % of oil yields were obtained under all the reaction conditions employed (runs 1-6). Gaseous products were mainly composed of methane (50-80 %) and carbon dioxide (10-30 %). Liquefaction of *Spirulina* under a nitrogen atmosphere without a catalyst gave 54.0 % of oil yield in 1-methylnaphthalene and 52.3 % in tetralin. Addition of Fe(CO)₅-S increased the oil yield to 63.7 and 66.9 % under a hydrogen atmosphere in 1-methylnaphthalene and tetralin, respectively. In the liquefaction under hydrogen without the catalyst (run 5), 0.28 wt% of hydrogen was absorbed from gas phase, whereas hydrogen consumption in the liquefaction increased to 1.2 wt% with the catalyst. Hydrogen activated on the dispersed catalyst might have contributed to increase the oil yield. Liquefaction of *Spirulina* in tetralin, a more efficient solvent for the liquefaction of woody biomass,¹ afforded similar conversion and product distribution as compare to those obtained in 1-methylnaphthalene. It is reported that tetralin is effective for the liquefaction of lignocellulose.⁸ However, *Spirulina* is mainly composed of proteins, thus fragment from *Spirulina* is considered to be stabilized easily even without a hydrogen donor. This is one of the characteristic differences between the liquefaction of micro algae and coal or woody biomass. Much smaller increases in the amount of hydrogen transferred to *Spirulina* would be accounted for the different mechanisms in the liquefaction of these two substances.

Effects of reaction temperature and reaction time in the liquefaction of *Spirulina*. Effects of reaction temperature on the product distribution in the liquefaction of *Spirulina* in tetralin is shown in Fig. 1 with or without catalyst. More than 90 % of conversions were obtained in the temperature range of 300-425 °C even without catalyst. Total yield of oil and gas increased from 46.8 to 80.4 % with increasing reaction temperature from 300 to 425 °C. Oil yield including water was 42.4 % at 300 °C and increased to 62.2 % at 400°C, but oil yield did not increase above 400 °C as compared to that at 400 °C, due to a large increase in the gas yields from 9.8 % at 400 °C to 13.9 % at 425 °C. Oil yield in the presence of catalyst showed similar tendencies, but effect of the catalyst was pronouncedly observed at 350 °C. Again remarkable increases in gas yields were observed above 400 °C. At a lower or a higher temperature, an addition of catalyst only slightly affected product distribution in the liquefaction of *Spirulina*.

Fig. 2 shows effects of reaction time on the product distribution in the liquefaction of *Spirulina* at 350 °C in tetralin without catalyst and with Fe(CO)₅-S. More than 90 % of conversions were obtained irrespective of reaction time and in the presence or absence of catalyst. Oil yield without

catalyst slightly increased from 46.8 to 53.6 % with increasing reaction time from 0 to 30 min. However, product distributions were almost constant for prolonged runs in the absence of catalyst. Oil yield with $\text{Fe}(\text{CO})_5\text{-S}$ increased from 52.3 to 66.9 % with increasing reaction time 0 to 60 min, further increase in the reaction time did not change product distribution. Slower reaction producing oil was promoted with the addition of a highly dispersed catalyst under hydrogen atmosphere.

Liquefaction in water. In practical process, drying wet *Spirulina* required a large quantity of energy. Thus liquefaction of *Spirulina* in wet form is desirable.

Spirulina was liquefied in 1-methylnaphthalene under carbon monoxide atmosphere with 0.5-2.0 g of water in the presence of $\text{Fe}(\text{CO})_5\text{-S}$ catalyst. The results are shown in Table 1 (runs 8-10). Gas yields were not measured, because major gaseous products from *Spirulina* are carbon monoxide and carbon dioxide, and they were masked with the charged carbon monoxide and the carbon dioxide produced according to the water gas shift reaction.

Addition of 0.5 g of water in the liquefaction of *Spirulina* with $\text{Fe}(\text{CO})_5\text{-S}$ under carbon monoxide afforded 74.5 % of oil yield (run 8). Oil plus gas yield of 75.5 % was obtained under hydrogen (run 6) with the same catalyst. Further increases in the amount of H_2O to 2.0 g (run 10) increased the oil plus gas yield to 83.1 %. Hydrogen produced was amounted to 2.1, 4.7, and 6.3 mmol after the reaction in the presence of 0.5, 1.0, and 2.0 g of water, respectively. Oil plus gas yields obtained with H_2O exceeded those obtained under hydrogen in 1-methylnaphthalene. The result that high oil yield of 64.3 % was obtained in 1-methylnaphthalene- H_2O mixed solvent (run 7) indicates that hydrolysis of *Spirulina* possibly occurred. Such behavior is quite different from coal and woody biomass liquefaction.

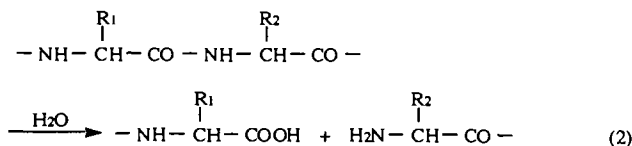
Spirulina was liquefied in water under nitrogen without catalyst in the temperature range of 200-350 °C (Fig. 3). Conversion increased from 71.8 to 93.5 % with increasing the reaction temperature from 200 to 350 °C. Gas yields were almost constant (6-8 %) in these temperature ranges. Oil yield increased from 48.4 to 78.3 % with increasing reaction temperature to 350 °C. However, conversion was slightly smaller than that obtained in 1-methylnaphthalene- H_2O mixed system under carbon monoxide with the catalyst.

Characterization of oil fractions. In order to eliminate contamination of the solvent, for the characterization of oil fractions, a more volatile solvent toluene was used in the liquefaction of *Spirulina*. The results are shown in Table 1 (runs 11-13). Similar tendencies in the liquefaction behavior were observed in toluene as compared to those obtained in 1-methylnaphthalene.

Elemental compositions of feed and oil fractions are shown in Table 2. Carbon contents of oil fractions obtained in toluene are 64.2-69.0 % and these values are higher than that of feed (46.1 %). Oxygen contents (by differences) of products were lowered to 14.0-19.9 % as compared to 41.4 % of feed. Oil fractions obtained in water showed lower carbon content of 57.3 % and consequently higher oxygen content of 28.5 %. Ratio of H/C in oil was almost constant irrespective of reaction conditions and decreased to 1.50-1.55 from 1.93 in the feed and ratio of O/C decreased to 0.15-0.37 from 0.67 in feed. These findings indicate that deoxygenation through dehydration or decarboxylation proceeded in the liquefaction of *Spirulina*.

Heating values of oil fractions were calculated according to the formula proposed by Ringen *et al.*⁷, using elemental composition. Heating values of oil fractions were higher than that of feed. Liquefaction of *Spirulina* in toluene gave oil fractions having heating values as high as 7700-7900 cal/g. Assuming water yield by the differences in the oxygen balance, 75.8 % and 71.1 % of heating values could be recovered as oil from the charged *Spirulina* having heating value of 4900 cal/g, in the liquefaction with or without $\text{Fe}(\text{CO})_5\text{-S}$ catalyst, respectively. Heating value of oil fraction obtained in water was 6200 cal/g and lower than that obtained in toluene, although a higher yield was obtained. Liquefaction in toluene with 1.0 g of water gave oil fraction not only in a high yield of 69.8 %, but also had a high heating value of 7300 cal/g. A presence of moderate amount of water is considered to be effective for the production of oil fraction having a high heating value in a high yield.

Fig. 4 shows FT-IR spectra of feed and oil fractions obtained in toluene and water with or without the Fe catalyst. Absorption at around 1652, 1545, and broad band 500-600 cm^{-1} ascribed to polypeptide in feed (a) are not seen in the spectrum of liquefied oil. This suggests that liquefaction of *Spirulina* proceeded by mainly scission of peptide linkages. Hydroxy or amine (3300 cm^{-1}), methyl and methylene (2800-3000, 1456, and 1389 cm^{-1}), and carbonyl (1705 and 1670 cm^{-1}) groups were confirmed by FT-IR spectra (b, c, and d). In the oil fraction obtained in water without the Fe catalyst (d), absorption peaks ascribed to carboxyl acid (3000-3300, 1705, and 1270 cm^{-1}) and amine (3300 and 1590 cm^{-1}) were more strongly observed as compared to the oil fraction obtained in toluene (b). This fact indicates that liquefaction of *Spirulina* proceeded via mainly hydrolysis of peptide linkages with water as shown in equation (2).



According to gel permeation chromatograms of the oil fractions prepared under different reaction conditions, molecular weights of oil fractions were distributed in broad range from 200 to 2000, showing peaks at 780 and 830. Since the evaporative light scattering detector was employed, detection of the low molecular weight component was limited to 200, possibility of the presence of lower molecular weight fraction can not be ruled out. Peaks at lower molecular weights region 400

and 490 were observed in the oil fractions obtained in toluene under hydrogen. Further increase in lower molecular weight product was observed in the liquefaction with the Fe catalyst. Thus the reactions to lower molecular weight product progressed through hydrocracking of C-C bonds with the catalyst under a hydrogen atmosphere.

These findings suggested that production of oil from *Spirulina* proceeded via mainly thermal decomposition or hydrolyses of peptide linkages with water fed or produced during liquefaction and hydrocracking of C-C bonds is promoted in the presence of a catalyst under hydrogen.

CONCLUSION

Liquefaction of *Spirulina* at 300-425 °C under hydrogen gave more than 90 % of conversions and 60 % of oil yields. Addition of Fe(CO)₅ catalyst increased oil yield from 52.3 to 66.9 % at 350 °C for 60 min in tetralin. Liquefaction in water gave oil yield as high as 78.3 % at 350 °C even under nitrogen atmosphere without the catalyst. Liquefaction in toluene gave oil fractions having high heating value of 7700-7900 cal/g, but the products containing large amount of oxygen estimated to have lower heating value of 6200 cal/g.

FT-IR and gel permeation chromatograph suggested that production of oil fractions mainly proceeded via thermal scission of polypeptide and hydrolysis with water, and further hydrocracking of C-C bond is promoted in the presence of Fe(CO)₅-S catalyst under hydrogen.

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Table 1 Results of the Liquefaction of *Spirulina* under Various Conditions

run	Solvent	H ₂ O (g)	Atmosphere	Catalyst	Conv.	Oil (%)	Gas	H ₂ -trans ^a (mmol)
1	TL		N ₂	none	91.9	52.3	5.2	0.3 ^b
2	TL		H ₂	none	92.2	54.2	7.2	4.5
3	TL		H ₂	Fe(CO) ₅ -S	92.0	66.9	6.2	5.6
4	1-MN		N ₂	none	88.1	54.0	5.2	0.1 ^b
5	1-MN		H ₂	none	91.8	54.4	8.9	2.8
6	1-MN		H ₂	Fe(CO) ₅ -S	94.9	63.7	11.8	11.7
7	1-MN	1.0	N ₂	none	95.4	64.3	9.7	0.6 ^b
8	1-MN	0.5	CO	Fe(CO) ₅ -S	96.1	74.5		2.1 ^b
9	1-MN	1.0	CO	Fe(CO) ₅ -S	96.6	79.0		4.7 ^b
10	1-MN	2.0	CO	Fe(CO) ₅ -S	97.8	83.1		6.3 ^b
11	TOL		H ₂	none	82.6	57.0	6.9	2.7
12	TOL		H ₂	Fe(CO) ₅ -S	90.1	63.3	4.1	3.6
13	TOL	1.0	N ₂	none	92.5	69.8	8.9	0.8 ^b
14	H ₂ O		N ₂	none	93.4	78.3	6.8	0.5 ^b

Reaction temperature 350 °C, reaction time 60 min, *Spirulina* 2.0 g, solvent 8.0 g, initial pressure 5 MPa, Fe(CO)₅ 1.0 mmol, S 2.0 mmol.

a) Amount of hydrogen transferred to products from gas phase and tetralin.

b) Amount of hydrogen produced after reaction.

Table 2 Elemental Analyses of Oil Fraction Products

run	C	H	N	O ^a	H/C	N/C	Heating Value (cal/g)
	46.1	7.4	4.8	41.4	1.93	0.09	4902
11	69.0	8.6	8.4	14.0	1.50	0.10	7939
12	66.7	8.6	7.5	16.2	1.55	0.10	7674
13	64.2	8.3	7.6	19.9	1.55	0.10	7284
14	57.3	7.4	6.8	28.5	1.55	0.10	6215

Reaction temperature 350 °C, reaction time 60 min, *Spirulina* 2.0 g, solvent 8.0 g, initial pressure 5 MPa, Fe(CO)₅ 1.0 mmol, S 2.0 mmol.

a) by differences

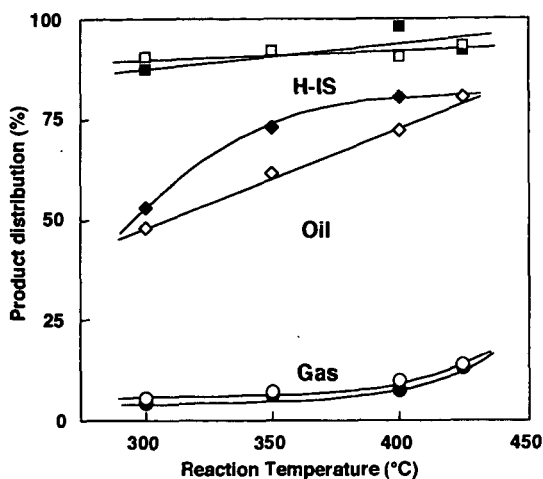


Fig.1 Effect of Reaction Temperature on the Product Distribution in the Liquefaction of Spirulina

Reaction time 60 min, Spirulina 2.0 g, TL 8.0 g,

PH₂ 5.0 MPa, Fe(CO)₅ 1.0 mmol, S 2.0 mmol

□ ◇ ○ without catalyst, ■ ◆ ● with Fe(CO)₅-S

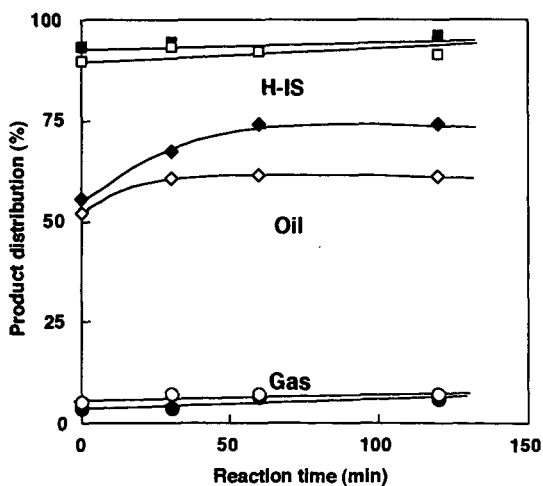


Fig.2 Effect of Reaction Time on the Product Distribution in the Liquefaction of Spirulina

Reaction temperature 350 °C, Spirulina 2.0 g, TL 8.0 g,

PH₂ 5.0 MPa, Fe(CO)₅ 1.0 mmol, S 2.0 mmol

□ ◇ ○ without catalyst, ■ ◆ ● with Fe(CO)₅-S

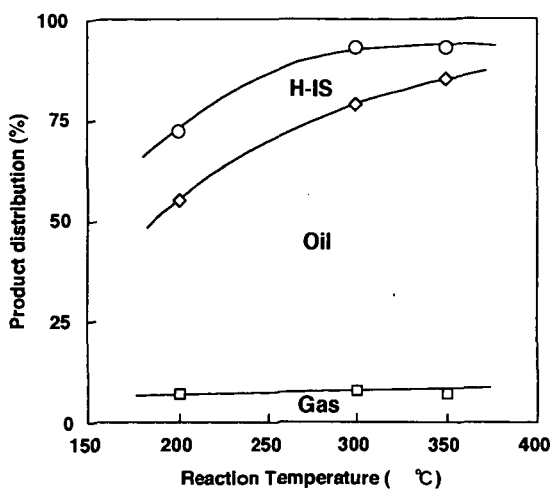


Fig.3 Effect of Reaction Temperature on the Product Distribution in the Liquefaction of Spirulina in water

Reaction time 60 min, Spirulina 2.0 g, H₂O 8.0 g, PN₂ 5.0 MPa

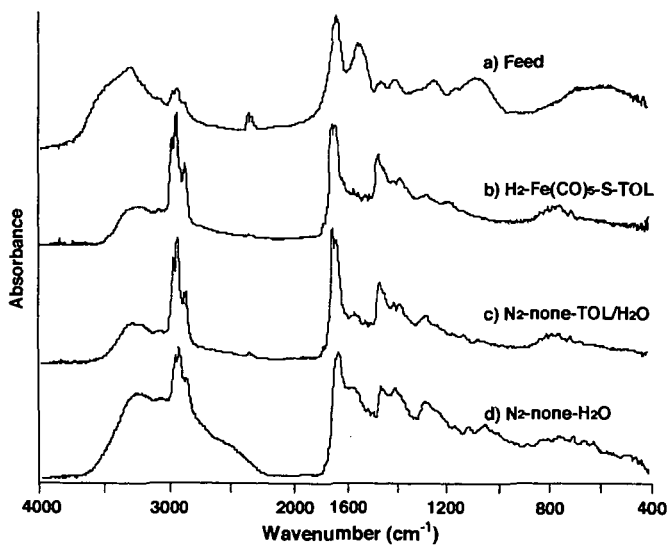


Fig.4 FT-IR Spectra of Spirulina and Liquefaction Products

Reaction temperature 350 °C, reaction time 60 min, Spirulina 2.0 g.
a) feed, b) PH₂ 5.0 MPa, toluene 8.0 g, Fe(CO)₅ 1.0 mmol, S 1.0 mmol,
c) PN₂ 5.0 MPa, toluene 8.0 g, H₂O 1.0 g, d) PN₂ 5.0 MPa, H₂O 1.0 g